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Synthesis of ferrocenyl- and hetaryl-substituted 2,2,2-trifluoroethanols and their conversion into 2,2,2-trifluoroethanethiols using Lawesson's reagent

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Keywords: Hetaryl ketones, Ferrocenyl ketones, Nucleophilic trifluoromathylation, Lawessons's reagent, Trifluoroethane thiols

ABSTRACT

Ferrocenyl- and hetaryl-substituted ketones react smoothly with the Ruppert-Prakash reagent and, after desilylation of the intermediate adduct, gave the corresponding tertiary 2,2,2-trifluoroethanols. Similarly, ferrocenyl carbaldehyde was converted into 1-ferrocenyl-2,2,2-trifluoroethanol via nucleophilic trifluoromethylation. Some of the obtained fluorinated alcohols were transformed into thiols by treatment with Lawesson's reagent or $P_2S_5 \cdot 2C_5H_5N$ complex. Remarkably, the obtained thiols are non-odorous compounds.

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[1] Part of the planned PhD thesis of R. H.-F., University of Łódź.

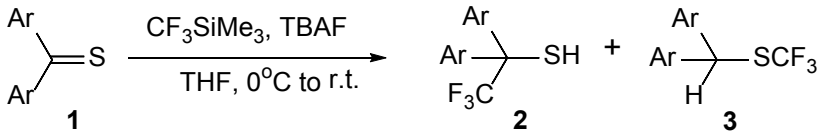
[2] Passed away on August 20th, 2015.

1. Introduction

Fluorinated alcohols and thiols are considered as an important class of fluorine containing building blocks useful for the preparation of more complex products of potential interest in medicinal chemistry, the crop protection industry, and materials science as well as for other applications, e.g. in the case of fluorinated alcohols, as nonconventional solvents [1]. The nucleophilic trifluoromethylation of aldehydes and ketones with Ruppert-Prakash reagent (CF_3SiMe_3) [2] opens a straightforward access to secondary and tertiary trifluoromethyl alcohols, respectively [3]. The asymmetric versions for these reactions are also known [4].

In spite of the fact that perfluorinated thiols are of great interest for materials chemistry [5], syntheses of trifluoromethyl thiols are scarcely reported. For example, nucleophilic substitution of 2,2,2-trifluoro-1,1-diphenylethane tosylate with H_2S at 50 ºC leads to 2,2,2-trifluoro-1,1-diphenylethanethiol in high yield [6]. Remarkably, the direct conversion of the corresponding alcohol into the thiol was achieved using Lawesson's reagent [7]. However, in that case, the reported yield was low (20%). In recent time, widely applied methods comprise Michael additions of 4-methoxyphenylmethanethiol onto 4,4,4-trifluorobut-2-enamides followed by debenzylation [8] or thioacetic acid onto 4,4,4-trifluorobut-2-en-1-ones followed by Et_3N-catalyzed ester cleavage [9]. In a modified procedure, thioacetic acid as the Michael donor can be replaced by H_2S [10].

In analogy to reactions with aromatic ketones, reactions of aromatic thioketones **1** with Rupert-Prakash reagent were also studied as a method for the preparation of tertiary trifluoromethyl thiols [11]. However, depending on the reaction conditions, mixtures of products were obtained, and the required thiols **2** were formed in low yields [11b]. In these reactions, the isomeric sulfides **3** were obtained as major products.

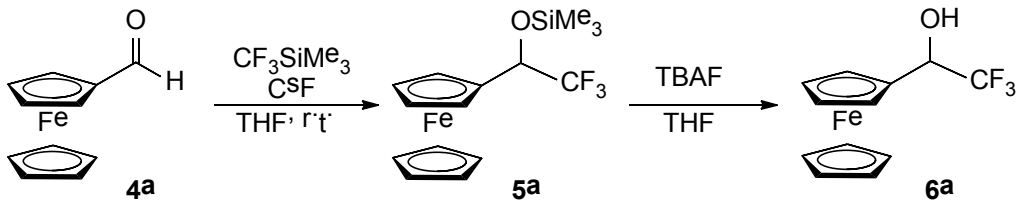


Scheme 1. Carbophilic vs thiophilic trifluoromethylation of aromatic thioketones [11b].

In recent publications we reported on the synthesis of hetaryl and ferrocenyl ketones and their conversions into the corresponding thioketones [12]. Preliminary experiments with Ruppert-Prakash reagent and phenyl thiophen-2-yl thioketone as well as ferrocenyl thiophen-2-yl thioketone gave complex mixtures of products. For that reason, we decided to elaborate a two-step procedure starting with the corresponding ketones. The first step was their nucleophilic trifluoromethylation leading efficiently to the trifluoromethyl alcohols, which subsequently were converted into hitherto unknown 2,2,2-trifluoroethanethiols.

2. Results and discussion

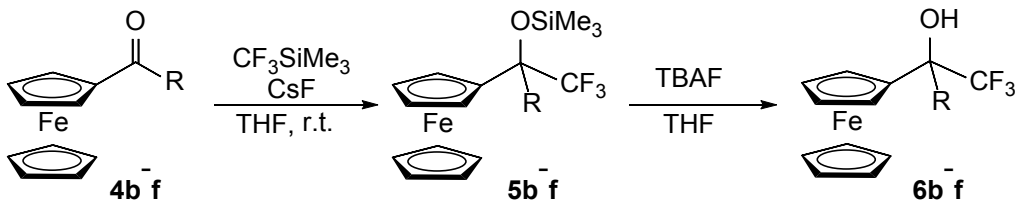
The first experiment was performed with ferrocenyl carbaldehyde **4a**, which under typical conditions (THF, room temperature, CsF as a catalyst) reacted smoothly with CF_3SiMe_3, to give the adduct **5a**. Subsequent desilylation by treatment with equimolar amounts of tetrabutylammonium fluoride (TBAF) led to 1-ferrocenyl-2,2,2-trifluoroethanol **6a** in high yield (Scheme 2, Table 1). The latter is a known compound [13], but now prepared for the first time by trifluoromethylation of **4a**.



Scheme 2. Reaction of ferrocenyl carbaldehyde (**4a**) with CF_3SiMe_3.

The asymmetric version of this reaction has also been studied in the presence of 15 mol% of a cinchonium salt as a catalyst. However, after desilylation and isolation of product **6a**, the HPLC analysis revealed a low *ee*-value of 28% only.

In a series of experiments with ferrocenyl ketones **4b-f**, the corresponding tertiary 2,2,2-trifluorethanols **6b-f** were obtained in high yields (60−80%, Scheme 3, Table 1). Remarkably, the attempted trifluoromethylation of the sterically crowded diferrocenyl ketone (**4g**), in spite of an extended reaction time, was unsuccessful. In all products of type **6**, the ^{13}C NMR spectra showed the quartet of the CF_3 group in a narrow range of 123.7-125.3 ppm with the characteristic $^1J_{CF}$ of ca. 280 Hz.

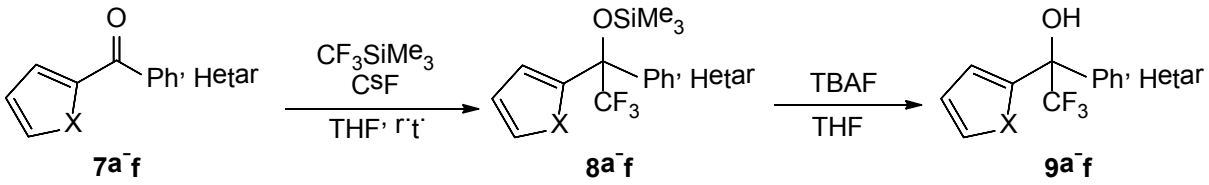


Scheme 3. Nucleophilic trifluoromethylation of ferrocenylketones **4b-f** (Table 1).

Table 1. 1-Ferrocenyl-2,2,2-trifluoroethanols **6** prepared via the nucleophilic trifluoromethylation of ferrocenyl carbaldehyde and ferrocenyl ketones **4**

Compound	R	Yield [%]
6a	H	84
6b	Furan-2-yl	73
6c	Selenophen-2-yl	71
6d	Thiophen-2-yl	62
6e	Methyl	80
6f	Phenyl	60

The trifluoromethylation reactions were extended to a group of hetaryl/phenyl and dihetaryl ketones **7a-f**. Also in this series, the reactions occurred smoothly at room temperature, and after desilylation of the intermediate silylethers **8**, the required products **9** were isolated in high yields (84−95%, Scheme 4, Table 2). Similarly, to the alcohols **6**, the ^{13}C NMR spectra of alcohols **9** showed the characteristic quartets of the CF_3 group. In addition, a singlet at ca. −78 ppm was registered in the ^{19}F NMR spectra.



Scheme 4. Nucleophilic trifluoromethylation of aryl/hetaryl ketones **7** (Table 2).

Table 2. 1-Hetaryl-1-phenyl- and 1,1-dihetaryl-2,2,2-trifluoroethanols **9**.

Compound	Ph, Hetar	C_4H_3X	Yield [%]
9a	Phenyl	Thiophen-2-yl	85
9b	Phenyl	Selenophen-2-yl	91
9c	Furan-2-yl	Thiophen-2-yl	85
9d	Furan-2-yl	Selenophen-2-yl	95
9e	Thiophen-2-yl	Thiophen-2-yl	84
9f	Selenophen-2-yl	Selenophen-2-yl	93

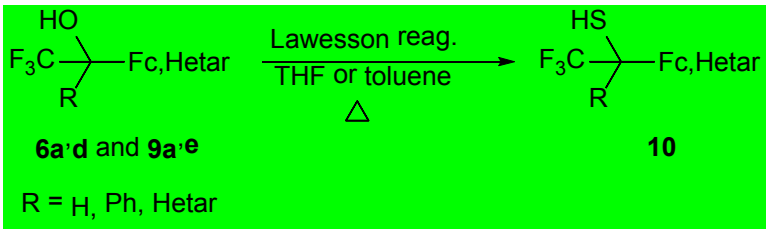
The unsuccessful attempts of the preparation of trifluoromethyl thiols via nucleophilic trifluoromethylation of thioketones (see: Introduction) prompted us to examine the reaction of selected alcohols **6** and **9** with Lawesson's reagent. It is well documented that the Lawesson's reagent is a powerful thionating agent for the conversion of C=O groups into C=S groups [13]. However, its application for the transformation of alcohols into thiols is also known, but the reported yields of the products vary remarkably, depending on the substitution pattern [14].

Heating of alcohols **6a**,**d**,**e** in THF and **9a**,**e** in toluene, respectively, in the presence of a slight excess of Lawesson's reagent resulted in their conversion to the corresponding thiols **10** in moderate yields (20–54% yield after chromatographic purification) (Scheme 5, Table 3). Their structures were confirmed by spectroscopic data. For example, the ^{1}H NMR spectrum of thiol **10c** showed a singlet at 3.21 ppm attributed to the SH group. In the ^{13}C NMR spectrum, two quartets located at 125.8 ppm ($^{1}J_{CF}$ = 280.5 Hz) and at 58.3 ppm ($^{2}J_{CF}$ = 29.4Hz), which correspond to the CF_3 group and the C(1) atom, respectively. Furthermore, the signal of the CF_3 group in the ^{19}F NMR spectrum was found at −69.5 ppm. Characteristically, the SH group absorbed in the IR spectrum at 2563 cm^{-1} with medium intensity.

In order to establish the scope and limitations of the conversion of the fluorinated alcohols of type **6** and **9** into the corresponding thiols, three alcohols bearing a furane ring, namely **6b**, **9c** and **9d**, were also tested in the reaction with Lawesson's reagent under typical conditions. In all cases, the expected thiols were isolated after chromatographic work-up only in trace amounts and the major part of the reaction mixtures consisted of non-identified decomposition products. Similarly, alcohols bearing a pyrrole ring, e.g., 1-phenyl-1-(pyrrol-2-yl)-2,2,2-trifluoroethanol, by treatment with Lawesson's reagent formed complex mixtures of non-identified products.

In search for an alternative thiolation procedure, the complex of P_2S_5 with pyridine ($P_2S_5 \cdot 2C_5H_5N$) [15] was tested in reactions with **9a** and **9e** in acetonitrile at 80 ºC. The expected thiols **10c** and **10d** were obtained in yields of ca. 30 and 50%, respectively. Thus, the applications of Lawesson's reagent and the P_2S_5 complex led to comparable results.

From the mechanistic point of view, the transformations of alcohols **6** and **9** into the corresponding thiols **10**, very likely occur via an intramolecular nucleophilic substitution in the intermediate adduct of the alcohol and the monomeric unit of Lawesson's reagent as suggested by Japanese authors [14].



Scheme 5. Thiolation of 1-ferrocenyl and 1-hetaryl-substituted 2,2,2-trifluoroethanols **6** and **9**.

Table 3. Ferrocenyl- and hetaryl-substituted 2,2,2-trifluoroethanethiols **10**

Compound	Fc, Hetar	R	Yield [%]
10a	Ferrocenyl	H	25
10b	Ferrocenyl	Thiophen-2-yl	20
10c	Ferrocenyl	Methyl	23
10d	Phenyl	Thiophen-2-yl	54
10e	Thiophen-2-yl	Thiophen-2-yl	43

3. Conclusions

The nucleophilic trifluoromethylation with the Ruppert-Prakash reagent can be applied successfully for the preparation of ferrocenyl- and hetaryl-substituted derivatives of 2,2,2-trifluoroethanol. These alcohols were converted into the corresponding thiols by treatment with Lawesson´s reagent in toluene or, alternatively,

using $P_2S_5 \cdot 2C_5H_5N$ in acetonitrile. The prepared fluorinated alcohols and thiols are new products and are attractive building blocks for the synthesis of more complex fluorinated organic compounds or for surface modification in materials chemistry. An interesting feature of the studied fluorinated thiols is that none of them displayed the typical unpleasant smell of alkanethiols. On the other hand, it is worth mentioning that some hetaryl-substituted ethanethiols are known as potent aroma compounds.

4. Experimental

4.1. General information

All solvents were dried over appropriate drying agents and distilled before use. Melting points were determined in a capillary using a Stewart® SMP30 and they are uncorrected. The IR spectra were recorded on a Nexus FT-IR spectrophotometer. The ^{1}H, ^{13}C and ^{19}F NMR were measured on a Bruker Avance III instrument (600, 150 and 565 MHz, respectively), using the solvent signal as reference. The elemental analyses were recorded on a Vario Micro Cube. HRMS (ESI) were recorded on a Bruker maXis spectrometer. Flash chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). The notation Fc in this study represents ferrocenyl. Applied ferrocenyl substituted and hetaryl substituted ketones were obtained by known methods according to the literature protocols [12]. Other reagents used in the present study were commercially available.

4.2. Synthesis of trifluoromethylated alcohols

Method A: Ferrocenyl substituted alcohols **6** *– general procedure*

A portion of ferrocenecarbaldehyde (**4a**) or ferrocenyl/hetaryl ketone **4b–f** (1mmol) was placed in the calcinated flask and dissolved in absolute THF (10 ml). Next, a catalytic amount of freshly dried CsF and a solution of Rupert-Prakash reagent (CF_3SiMe_3; 1.2 mmol, 0.17 g) in THF (1 ml) were added under inert gas atmosphere. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the solvent was evaporated and crude products were purified by FCC (CH_2Cl_2/MeOH 99:1). The obtained silylated ether **5** was dissolved in THF (5 ml) and the flask was placed in an ice bath (0 °C). Then, tetrabutylammonium fluoride

(TBAF; 1.2 ml, 1M solution) was added; the mixture was stirred until all of the ferrocenyl substituted silylated ether was consumed. After completion of reaction, water (15 ml) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated. The crude product was purified by FCC (CH_2Cl_2/MeOH 99:1). This reaction can be carried out without isolation of the intermediate, silylated ether, but in that case, the yield of **6** was significantly lower.

1-Ferrocenyl-2,2,2-trifluoroethanol (**6a**). Yield: 238 mg (84%), yellow solid, m.p. 73.2–74.8 ºC. IR (KBr, cm^{-1}): *υ* 3463*s* (OH), 3098*m*, 2924*m*, 2853*m*, 2252*w*, 2057*w*, 1654*m*, 1411*m*, 1393*m*, 1353*m*, 1275*vs*, 1246*vs*, 1184*vs*, 1119*vs*, 1072*s*, 1027*s*, 1000m, 843*s*, 814*s*, 777*m*, 692*s*, 501*s*, 484*s*, 460*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.53 (d, 1H, $^3J_{H,H}$ = 5.4 Hz, OH), 4.27 (s, 5H, 5CH-Fc), 4.28 (br s, 2H, 2CH-Fc), 4.34 (br s, 1H, CH-Fc), 4.41 (br s, 1H, CH-Fc), 4.64–4.68 (m, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 66.0, 68.7, 68.8, 68.9 (9 CH-Fc), 69.2 (q, $^2J_{CF}$ = 32.4 Hz, CH), 83.5 (C_q-Fc), 123.9 (q, $^1J_{CF}$ = 280.5 Hz, CF_3). ^{19}F NMR (565 MHz, $CDCl_3$): δ –78.1 (d, $^3J_{HF}$ = 6.2 Hz, CF_3). HRMS (ESI): *m/z* calcd. for $C_{12}H_{11}F_3FeO$ 284.01059; found 284.01043.

1-Ferrocenyl-1-(furan-2-yl)-2,2,2-trifluoroethanol (**6b**). Yield: 255 mg (73%), yellow solid, m.p. 64.0–66.0 ºC. IR (KBr, cm^{-1}): *υ* 3520*m* (OH), 3156*w*, 3138*w*, 3109*m*, 3099*m*, 1647*w*, 1505*m*, 1411*m*, 1383*m*, 1363*m*, 1265*m*, 1242*m*, 1216*vs*, 1173*vs*, 1147*vs*, 1106*m*, 1094*s*, 1068*m*, 1046*m*, 1011*s*, 972*m*, 934*m*, 881*m*, 826*s*, 743*s*, 653*m*, 599*m*, 499*s*, 486*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.34 (s, 1H, OH), 4.20 (s, 5H, 5CH-Fc), 4.27–4.28 (m, 1H, CH-Fc), 4.28–4.29 (m, 1H, CH-Fc), 4.30–4.31 (m, 1H, CH-Fc), 4.52–4.53 (m, 1H, CH-Fc), 6.46 (dd, 1H, $^3J_{H,H}$ = 1.8 Hz, $^3J_{H,H}$ = 3.0 Hz, $CH_{arom.}$), 6.53 (d, 1H, $^3J_{H,H}$ = 3.0 Hz, $CH_{arom.}$), 7.50 (dd, 1H, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 0.6 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 68.6, 68.8, 68.9, 69.0 (9 CH-Fc), 74.0 (q, $^2J_{CF}$ = 30.9 Hz, C_q), 88.1 (C-Fc), 108.8, 110.5, 142.5 (3 $CH_{arom.}$), 123.7 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 151.0 ($C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ –77.9 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{13}F_3FeO_2$ 350.02116; found 350.02092.

1-Ferrocenyl-1-(selenophen-2-yl)-2,2,2-trifluoroethanol (**6c**). Yield: 293 mg (71%), yellow solid, m.p. 70.5–71.9 ºC. IR (KBr, cm^{-1}): *υ* 3489*m* (OH), 3115*w*, 3095*w*, 3060*w*, 1654*w*, 1637*w*, 1450*m*, 1412*w*, 1381*w*, 1335*m*, 1285*m*, 1210*m*, 1178*vs*, 1167*vs*, 1106*m*, 1076*m*, 1028*m*, 1002*m*, 934*m*, 876*m*, 847*m*, 823*m*, 781*m*, 725*m*, 695*m*, 497*m*, 487*m*, 461*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.69 (s, 1H, OH), 4.25–4.27 (m, 2H, 2CH-

Fc), 4.28 (s, 5H, 5CH-Fc), 4.36–4.37 (m, 1H, CH-Fc), 4.54–4.55 (m, 1H, CH-Fc), 7.15 (br d, $^{3}J_{H,H}$ = 3.6 Hz, 1H, $CH_{arom.}$), 7.25 (dd, 1H, $^{3}J_{H,H}$ = 5.4 Hz, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 8.00 (dd, 1H, $^{4}J_{H,H}$ = 1.2 Hz, $^{3}J_{H,H}$ = 5.4 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 68.3, 68.7, 68.9, 69.0 (9 CH-Fc), 76.2 (q, $^{2}J_{CF}$ = 30.5 Hz, C_q), 91.2 (C-Fc), 124.2 (q, $^{1}J_{CF}$ = 284.6 Hz, CF_3), 128.1, 129.4, 130.9 (3 $CH_{arom.}$), 149.2 ($C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ –77.20 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{13}F_3FeOSe$ 413.94277; found 413.94281.

1-Ferrocenyl-1-(thiophen-2-yl)-2,2,2-trifluoroethanol (**6d**). Yield: 227 mg (62%), yellow solid, m.p. 73.3–75.1 ºC. IR (KBr, cm^{-1}): *υ* 3501*s* (OH), 3119*m*, 3096*m*, 3073*m*, 2924*w*, 2854*w*, 1636*w*, 1436*m*, 1412*m*, 1381*m*, 1342*m*, 1261*s*, 1210*s*, 1179*vs*, 1167*vs*, 1106*m*, 1079*s*, 1057*m*, 1029*s*, 1001*m*, 935*m*, 887*m*, 858*m*, 842*m*, 822*s*, 728*s*, 707*s*, 638*m*, 580*m*, 525*m*, 497*m*, 479*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.58 (s, 1H, OH), 4.21–4.22 (m, 1H, CH-Fc), 4.26 (s, 5H, 5CH-Fc), 4.27–4.28 (m, 1H, CH-Fc), 4.35–4.36 (m, 1H, CH-Fc), 4.55–4.56 (m, 1H, CH-Fc), 7.01 (dd, 1H, $^{3}J_{H,H}$ = 5.4 Hz, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.02–7.03 (m, 1H, $CH_{arom.}$), 7.32 (dd, 1H, $^{4}J_{H,H}$ = 1.2 Hz, $^{3}J_{H,H}$ = 4.8 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 68.5, 68.8, 68.9, 69.0 (9 CH-Fc), 75.1 (q, $^{2}J_{CF}$ = 30.6 Hz, C_q), 91.1 (C-Fc), 124.2 (q, $^{1}J_{CF}$ = 284.4 Hz, CF_3), 125.4, 126.1, 126.8 (3 $CH_{arom.}$), 142.3 ($C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −77.6 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{13}F_3FeOS$ 365.99831; found 365.99823.

1-Ferrocenyl-1-methyl-2,2,2-trifluoroethanol (**6e**). Yield: 238 mg (80%), yellow solid, m.p. 52.0–54.0 ºC. IR (KBr, cm^{-1}): *υ* 3535*s* (OH), 3104*m*, 3094*m*, 3003*m*, 2949*w*, 2851*w*, 1647*w*, 1448*m*, 1410*m*, 1385*m*, 1359*m*, 1274*m*, 1169*vs*, 1131*s*, 1076*s*, 1033*s*, 1008*m*, 897*m*, 821*m*, 808*m*, 710*m*, 682*m*, 504*m*, 485*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.70 (s, 3H, CH_3), 2.64 (s, 1H, OH), 4.28 (s, 8H, 8CH-Fc), 4.41 (s, 1H, CH-Fc). ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.8 (CH_3), 66.3, 66.4, 67.8, 68.5, 68.7, 68.8 (9 CH-Fc), 72.3 (q, $^{2}J_{CF}$ = 29.3 Hz, C_q), 90.0 (C_q-Fc), 125.3 (q, $^{1}J_{CF}$ = 283.8 Hz, CF_3). ^{19}F NMR (565 MHz, $CDCl_3$): δ −81.4 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{13}H_{13}F_3FeO$ 298.02624; found 298.02619.

1-Ferrocenyl-1-phenyl-2,2,2-trifluoroethanol (**6f**). Yield: 216 mg (60%), yellow solid, m.p. 112.0–113.0 ºC. IR (KBr, cm^{-1}): *υ* 3493*m* (OH), 3091*w*, 3072*w*, 2955*w*, 2923*w*, 2857*w*, 1654*w*, 1492*m*, 1448*m*, 1413*m*, 1369*m*, 1350*m*, 1283*m*, 1217*m*, 1163*vs*, 1109*m*, 1065*m*, 1027*m*, 1002*m*, 970*m*, 913*m*, 850*m*, 821*m*, 761*m*, 726*vs*, 694*m*, 656*m*, 511*m*, 489*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.54 (s, 1H, OH), 4.04 (br s, 1H, CH-Fc), 4.24 (br s, 1H, CH-Fc), 4.31 (s, 5H, 5CH-Fc), 4.41 (br s, 1H, CH-Fc), 4.61 (br s, 1H,

CH-Fc), 7.31–7.33 (m, 3H, 3 $CH_{arom.}$), 7.45–7.47 (m, 2H, 2 $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.3, 68.2, 68.3, 68.5, 68.8, 68.9 (9 CH-Fc), 75.3 (q, $^2J_{CF}$ = 29.1 Hz, C_q), 92.9 (C_q-Fc), 124.9 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 127.2, 127.6, 128.2 (5 $CH_{arom.}$), 138.4 ($C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −76.6 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{18}H_{15}F_3FeO$ 360.04189; found 360.04187.

Method B: Hetaryl substituted alcohols **9** *– general procedure*

The corresponding ketone was placed in a calcinated flask and dissolved in THF (2 ml). Then, a catalytic amount of freshly dried CsF and a solution of Rupert-Prakash reagent (1.2 mmol, 0.17 g) in THF (1 ml) were added under inert gas atmosphere. The mixture was stirred at 0 ºC for 1 h. After this time, TBAF (1.2 ml, 1M solution) was added and the solution was stirred overnight. The subsequent work-up procedure was analogous to the one described for alcohols **6**. Crude product was purified by chromatography (hexane/CH_2Cl_2 1:1).

1-Phenyl-1-(thiophen-2-yl)-2,2,2-trifluoroethanol (**9a**). Yield: 220 mg (85%), yellow solid, m.p. 39.0–45.0 ºC. IR (KBr, cm^{-1}): *υ* 3536*s* (OH), 3107*w*, 3064*w*, 3034*w*, 1603*w*, 1497*m*, 1450*s*, 1434*m*, 1339*m*, 1275*s*, 1231*s*, 1163*s*, 1049*s*, 935*m*, 914*m*, 879*m*, 839*m*, 763*m*, 719*s*, 698*s*, 672*m*, 646*m*, 542*m*. ^1H NMR (600 MHz, $CDCl_3$): δ 3.08 (s, 1H, OH), 7.02 (dd, 1H, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.20–7.23 (m, 1H, $CH_{arom.}$), 7.36 (dd, 1H, $^3J_{H,H}$ = 4.8 Hz, $^4J_{H,H}$ = 1.2 Hz, $CH_{arom.}$), 7.37–7.41 (m, 3H, 3 $CH_{arom.}$), 7.59–7.63 (m, 2H, 2 $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 77.8 (q, $^2J_{CF}$ = 29.9 Hz, C_q), 124.8 (q, $^1J_{CF}$ = 284.6 Hz, CF_3), 126.8, 126.9, 127.0, 127.2, 128.2, 129.0 (8 $CH_{arom.}$), 137.8, 143.2 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −76.3 (s, CF_3). MS (ESI): *m/z* 257 (100, $[M–1]^-$). Anal. calcd. for $C_{12}H_9F_3OS$ (258.26): C, 55.81; H, 3.51; S 12.42%. Found: C, 55.72; H, 3.68; S, 12.30%.

1-Phenyl-1-selenophen-2-yl-2,2,2-trifluoroethanol (**9b**). Yield: 277 mg (91%), yellow solid, m.p. 52.0–54.0 ºC. IR (KBr, cm^{-1}): *υ* 3525*s* (OH), 3106*w*, 1490*w*, 1449*m*, 1354*m*, 1273*s*, 1166*vs*, 1073*m*, 1059*m*, 1040*m*, 935*m*, 913*m*, 857*m*, 838*m*, 768*m*, 715*s*, 701*s*, 667*m*, 646*m*, 564*m*, 528*m*, 421*m*. ^1H NMR (600 MHz, $CDCl_3$): δ 3.13 (s, 1H, OH), 7.26 (dd, 1H, $J_{H,H}$ = 4.8 Hz, $J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.37–7.39 (m, 1H, $CH_{arom.}$), 7.40–7.42 (m, 3H, 3 $CH_{arom.}$), 7.63–7.67 (m, 2H, 2 $CH_{arom.}$), 8.07 (dd, 1H, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 1.2 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 79.1 (q, $^2J_{CF}$ = 29.6 Hz, C_q), 124.7 (q, $^1J_{CF}$ = 285.0 Hz, CF_3), 126.9, 128.2, 129.0, 129.2, 129.3, 132.5 (8 $CH_{arom.}$), 138.2, 150.0 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −76.0 (s, CF_3). MS

(ESI): *m/z* 305 (100, $[M]^-$). Anal. calcd. for $C_{12}H_9F_3OSe$ (305.15): C, 47.23; H, 2.97%. Found: C, 47.30; H, 3.20%.

1-(Furan-2-yl)-1-(thiophen-2-yl)-2,2,2-trifluoroethanol (**9c**). Yield: 211 mg (85%), yellow oil. IR (film, cm^{-1}): *υ* 3528*s* (OH), 3126*w*, 1616*w*, 1498*m*, 1434*m*, 1344*m*, 1275*m*, 1225*m*, 1178*s*, 1150*s*, 1063*m*, 1046*m*, 1018*m*, 958*m*, 893*m*, 884*m*, 831*m*, 746*m*, 729*m*, 708*m*, 596*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.44 (s, 1H, OH), 6.40–6.44 (m, 1H, $CH_{arom.}$), 6.51 (d, 1H, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.04 (t, 1H, $^3J_{H,H}$ = 4.8 Hz, $CH_{arom.}$), 7.19 (d, 1H, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.38 (d, 1H, $^3J_{H,H}$ = 5.4 Hz, $CH_{arom.}$), 7.47 (br s, 1H, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 75.0 (q, $^2J_{CF}$ = 32.0 Hz, C_q), 110.3, 110.7, 126.8, 127.0, 127.1, 143.6 (6 $CH_{arom.}$), 123.8 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 139.3, 149.8 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −78.3 (s, CF_3). MS (ESI): *m/z* 247 (100, $[M–1]^-$). Anal. calcd. for $C_{10}H_7F_3O_2S$ (248.22): C, 48.39; H, 2.84; S, 12.92%. Found: C, 48.15; H, 3.05; S, 13.00%.

1-(Furan-2-yl)-1-(selenophen-2-yl)-2,2,2-trifluoroethanol (**9d**). Yield: 280 mg (95%), yellow oil. IR (film, cm^{-1}): *υ* 3523*s* (OH), 3126*w*, 3064*w*, 2960*w*, 2926*w*, 2850*w*, 1709*w*, 1615*w*, 1544*w*, 1498*m*, 1449*m*, 1351*m*, 1270*s*, 1225*s*, 1177*vs*, 1151*vs*, 1070*m*, 1038*m*, 1017*m*, 957*m*, 883*m*, 835*m*, 780*m*, 745*s*, 726*s*, 696*s*, 595*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.53 (s, 1H, OH), 6.43 (dd, 1H, $^3J_{H,H}$ = 1.8 Hz, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 6.53 (d, 1H, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.29 (dd, 1H, $^3J_{H,H}$ = 5.4 Hz, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.35–7.37 (m, 1H, $CH_{arom.}$), 7.49 (dd, 1H, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 0.6 Hz, $CH_{arom.}$), 8.09 (dd, 1H, $^3J_{H,H}$ = 5.4 Hz, $^4J_{H,H}$ = 1.2 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.2 (q, $^2J_{CF}$ = 31.8 Hz, C_q), 110.2, 110.7, 129.0, 129.5, 132.4, 143.6 (6 $CH_{arom.}$), 123.6 (q, $^1J_{CF}$ = 284.4 Hz, CF_3), 145.8, 149.9 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ –78.2 (s, CF_3). Anal. calcd. for $C_{10}H_7F_3O_2Se$ (295.12): C, 40.70; H, 2.39%. Found: C, 40.64; H, 2.22%.

1,1-Di(thiophen-2-yl)-2,2,2-trifluoroethanol (**9e**). Yield: 222 mg (84%), yellow oil. IR (film, cm^{-1}): *υ* 3521*m* (OH), 3108*w*, 1810*w*, 1614*w*, 1528*w*, 1433*m*, 1362*m*, 1332*m*, 1277*m*, 1231*m*, 1173*s*, 1082*m*, 1036*m*, 894*m*, 874*m*, 832*m*, 720*s*, 706*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.27 (s, 1H, OH), 7.04 (dd, 2H, $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 3.6 Hz, 2 $CH_{arom.}$), 7.24–7.26 (m, 2H, 2 $CH_{arom.}$), 7.39 (dd, 2H, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 5.4 Hz, 2 $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.7 (q, $^2J_{CF}$ = 31.5 Hz, C_q), 124.3 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 126.9, 127.0, 127.2 (6 $CH_{arom.}$), 141.9 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −71.7 (s, CF_3). MS (ESI): *m/z* 247 (100, $[M–OH]^+$). Anal. calcd. for

$C_{10}H_7F_3OS_2$ (264.29): C, 45.45; H, 2.67; S, 24.27%. Found: C, 45.21; H, 2.96; S, 24.23%.

1,1-Di(selenophen-2-yl)-2,2,2-trifluoroethanol (**9f**). Yield: 332 mg (93%), yellow oil. IR (film, cm^{-1}): υ 3509*s* (OH), 3101*w*, 3062*w*, 2928*w*, 1812*w*, 1706*w*, 1589*m*, 1522*m*, 1446*m*, 1421*m*, 1344*m*, 1331*m*, 1270*s*, 1229*s*, 1173*vs*, 1077*m*, 1036*m*, 878*m*, 827*m*, 793*m*, 769*m*, 716*vs*, 695*vs*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.50 (s, 1H, OH), 7.28 (dd, 2H, $^3J_{H,H}$ = 5.4 Hz, $^3J_{H,H}$ = 3.6 Hz, 2 $CH_{arom.}$), 7.43–7.46 (m, 2H, 2 $CH_{arom.}$), 8.08 (dd, 2H, $^3J_{H,H}$ = 5.4 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 79.1 (q, $^2J_{CF}$ = 30.8 Hz, C_q), 124.0 (q, $^1J_{CF}$ = 284.6 Hz, CF_3), 129.2, 129.4, 132.5 (6 $CH_{arom.}$), 148.9 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −77.5 (s, CF_3). Anal. calcd. for $C_{10}H_7F_3OSe_2$ (358.08): C, 33.54; H, 1.97%. Found: C, 33.77; H, 2.06%.

4.3. Synthesis of fluorinated thiols **10**

Method A: Ferrocenyl substituted thiols **10a–c** *– general procedure*

To a the solution of the corresponding trifluoromethylated alcohol **6** (1 mmol) in THF (5 ml), Lawesson's reagent (LR) (0.6 mmol, 0.24 g) was added and the obtained solution was magnetically stirred and heated to reflux for 5 h. Then, the solvent was evaporated and the crude product was purified by FCC (CH_2Cl_2/hexane 3:7).

1-Ferrocenyl-2,2,2-trifluoroethanethiol (**10a**). Yield: 75 mg (25%), yellow oil. IR (film, cm^{-1}): υ 3096*w*, 2927*w*, 2854*w*, 2572*w*, 1412*w*, 1316*m*, 1256*vs*, 1237*m*, 1151*s*, 1108*vs*, 1043*m*, 1030*m*, 824*m*, 672*m*, 617*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.48 (d, 1H, $^3J_{H,H}$ = 6.0 Hz, SH), 4.21–4.23 (m, 1H, CH-Fc), 4.26 (br s, 6H, 6CH-Fc), 4.31–4.35 (m, 2H, 2CH), 4.38 (br s, 1H, CH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 42.6 (q, $^2J_{CF}$ = 31.6 Hz, CH), 67.4, 68.3, 68.6, 69.4, 69.5 (9 CH-Fc), 81.3 (d, $J_{H,H}$ = 1.5 Hz, C_q-Fc), 124.8 (q, $^1J_{CF}$ = 277.3 Hz, CF_3). ^{19}F NMR (565 MHz, $CDCl_3$): δ −71.6 (d, $^3J_{HF}$ = 6.2 Hz, CF_3). HRMS (ESI): *m/z* calcd. for $C_{12}H_{11}F_3FeS$ 299.98775; found 299.98750.

1-Ferrocenyl-1-(thiophen-2-yl)-2,2,2-trifluoroethanethiol (**10b**). Yield: 76 mg (20%), yellow oil. IR (film, cm^{-1}): υ 3097*m*, 2926*m*, 2854*m*, 1689*w*, 1628*w*, 1459*w*, 1434*m*, 1362*w*, 1333*m*, 1319*m*, 1300*m*, 1248*vs*, 1230*s*, 1164*vs*, 1147*vs*, 1125*s*, 1105*vs*, 1043*m*, 1030*m*, 1001*m*, 869*m*, 818*s*, 789*m*, 709*vs*, 650*m*, 605*m*, 543*m*, 484*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.01 (s, 5H, 5CH-Fc), 4.19–4.20 (m, 1H, CH-Fc), 4.21–4.22 (m, 1H, CH-Fc), 4.24 (br s, 1H, CH-Fc), 4.33 (br s, 1 CH-Fc), 4.67 (q, $J_{H,H}$ = 9.0 Hz, SH), 7.06 (dd, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 4.8 Hz, $CH_{arom.}$), 7.14 (d, 1H, $^3J_{H,H}$ = 3.0 Hz, $CH_{arom.}$),

7.33 (d, 1H, $^{3}J_{H,H}$ = 4.8 Hz, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 46.4 (q, $^{2}J_{CF}$ = 29.0 Hz, C_q), 68.0, 68.3, 68.4, 69.1, 69.2, 69.8 (9 CH-Fc), 82.4 (d, $J_{H,H}$ = 2.0 Hz, C_q-Fc), 125.0 (q, $^{1}J_{CF}$ = 279.6 Hz, CF_3), 125.2, 126.5, 127.6 (3 $CH_{arom.}$), 137.0 ($C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −69.9 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{16}H_{13}F_3FeS_2$ 381.97679; found 381.97603.

1-Ferrocenyl-1-methyl-2,2,2-trifluoroethanethiol (**10c**). Yield: 72 mg (23%), yellow oil. IR (film, cm^{-1}): υ 3104*w*, 2990*w*, 2949*w*, 2585*w*, 2360*w*, 1632*w*, 1454*m*, 1416*w*, 1378*m*, 1274*s*, 1252*s*, 1166*s*, 1144*s*, 1109*m*, 1081*s*, 1033*m*, 1005*m*, 891*m*, 834*m*, 815*m*, 770*m*, 688*m*, 644*m*, 495*s*, 473*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.92 (s, 3H, CH_3), 2.70 (br s, 1H, SH), 4.23 (br s, 1H, CH-Fc), 4.24–4.33 (m, 7H, 7CH-Fc), 4.41(br s, 1H, CH-Fc). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.3 (CH_3), 50.0 (q, $^{2}J_{CF}$ = 28.5 Hz, C_q), 68.1, 68.6, 69.3 (9 CH-Fc), 87.8 (br s, C_q-Fc), 126.2 (q, $^{1}J_{CF}$ = 280.2 Hz, CF_3). ^{19}F NMR (565 MHz, $CDCl_3$): δ −76.7 (s, CF_3). HRMS (ESI): *m/z* calcd. for $C_{13}H_{13}F_3FeS$ 314.00340; found 314.00276.

Method B: Hetaryl substituted thiols **10d–e** *– general procedure*

To the solution of a corresponding trifluoromethylated alcohol **9** (1 mmol) in toluene (5 ml) or acetonitrile, Lawesson's reagent (LR) (0.6 mmol, 0.24 g) or $P_2S_5{\cdot}2C_5H_5N$ was added under inert gas atmosphere. The mixture was stirred at reflux, and progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated and the crude product was purified by column chromatography (pentane/ethyl acetate 9:1).

1-Phenyl-1-(thiophen-2-yl)-2,2,2-trifluoroethanethiol (**10d**). Yield: 148 mg (54%), yellow oil. IR (film, cm^{-1}): υ 3106*w*, 3065*w*, 3038*w*, 2926*w*, 2853*w*, 2563*w*, 1955*w*, 1807*w*, 1600*w*, 1497*m*, 1448*m*, 1432*m*, 1247*vs*, 1166*vs*, 1112*m*, 1082*m*, 1052*m*, 1037*m*, 974*m*, 897*m*, 876*m*, 832*m*, 747*m*, 704*vs*, 656*m*, 540s. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.24 (s, 1H, SH), 6.99–7.03 (m, 1H, $CH_{arom.}$), 7.20–7.23 (m, 1H, $CH_{arom.}$), 7.33–7.39 (m, 5H, 5 $CH_{arom.}$), 7.51–7.55 (m, 1H, $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 58.3 (q, $^{2}J_{CF}$ = 29.4 Hz, C_q), 125.8 (q, $^{1}J_{CF}$ = 280.4 Hz, CF_3), 126.6, 126.9, 128.2, 128.3, 128.4, 128.8 (8 $CH_{arom.}$), 138.4, 144.1 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −69.6 (s, CF_3). Anal. calcd. for $C_{12}H_9F_3S_2$ (274.33): C, 52.54; H, 3.31; S, 23.3%. Found: C, 52.41; H, 3.58; S, 23.16%.

1,1-Ditiophen-2-yl-2,2,2-trifluoroethanethiol (**10e**). Yield: 121 mg (43%), yellow oil. IR (film, cm^{-1}): υ 3108*w*, 2923*w*, 2552*w*, 1804*w*, 1733*w*, 1607*w*, 1539*w*,

1431*m*, 1370*w*, 1334*m*, 1322*m*, 1254*vs*, 1163*vs*, 1114*s*, 1096*m*, 1070*m*, 1047*m*, 857*m*, 829*m*, 782*m*, 764m, 704*vs*, 612*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.51 (s, 1H, SH), 7.02 (dd, 2H, $^{3}J_{H,H}$ = 5.4 Hz, $^{3}J_{H,H}$= 3.6 Hz, 2 $CH_{arom.}$), 7.25–7.27 (m, 2H, 2 $CH_{arom.}$), 7.35 (dd, 2H, $^{3}J_{H,H}$ = 5.4 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 2 $CH_{arom.}$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.3 (q, $^{2}J_{CF}$ = 31.1 Hz, C_q), 125.4 (q, $^{1}J_{CF}$ = 280.4 Hz, CF_3), 126.9, 127.1, 128.3, 128.4 (6 $CH_{arom.}$), 142.6 (2 $C_{arom.}$). ^{19}F NMR (565 MHz, $CDCl_3$): δ −72.2 (s, CF_3). Anal. calcd. for $C_{10}H_7F_3S_3$ (280.35): C, 42.84; H, 2.52; S, 34.31%. Found: C, 42.96; H, 2.66; S, 34.30%.

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